# Charge transport in a $\pi$-conjugated polymer: Generalized Langevin equation analysis

Seong Hyun Kim,* Taehyoung Zyung, Hye Yong Chu, Lee-Mi Do, and Do-Hoon Hwang

*Electronics and Telecommunications Research Institute, Kajeong, Yusong, Taejon 305-350, Korea*

The complex dielectric constants of polymer light-emitting diodes using poly [2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] were measured, and the generalized Langevin equation was used to analyze the dielectric behavior in the frequency domain. We also proposed appropriate fitting functions for the voltage dependence of the fitting parameters. We confirmed that the generalized Langevin equation offers a very good approach to analyze and understand the transport properties of charge carriers in a $\pi$-conjugated polymer.

A typical polymer light-emitting diode (LED) consists of a thin layer of conjugated polymer sandwiched between two electrodes on top of a glass substrate. Under forward dc bias, electrons and holes are injected from the cathode and the anode, respectively, into the polymer. The injected charge carriers move through the polymer due to the applied external electric field over a certain distance until recombination takes place. Thus the operation of the polymer LED could be considered in three processes: injection, transport, and recombination of the charges.[1]

To improve the performance of polymer LED's, it is vital to understand which mechanism(s) control(s) the current density-voltage (*J-V*) characteristics of a given device structure.[2] Transport at dc or at very low frequencies requires a kind of percolating network of transition, in which the weakest links (intrachain connection) determine the magnitude of the conductivity. At highfrequencies, the charge carriers become localized in small regions of low-energy barriers. In this context, studying the conductivity in the frequency domain is essential due to its spectroscopic character. In practice also, for the pulse operation of the LED, we have to understand the current-voltage (*I-V*) characteristics in the frequency domain, i.e., the relaxation process should be studied.

Recently, ionic motions in amorphous $LiNbO_3, KNbO_3$, and $PbTiO_3$ were described by using a modified generalized Langevin equation.[3] In this article, we analyzed the frequency-dependent dielectric constant of an indium tin oxide (ITO)-poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV)-aluminum (Al) device using the generalized Langevin equation. Based on the results of this analysis, the conduction mechanism of the charge carrier is discussed.

Polymer films were obtained by spin coating the filtered polymer solution onto the substrates with an ITO electrode. Then the polymer films on the ITO/glass substrates were subjected to a heat treatment in a vacuum oven for an hour. Aluminum was vapor deposited as the cathode at a working pressure below $4 \times 10^{-6}$ Torr, yielding an active size of 5-mm diameter. The *I-V* characteristics and the impedances of the samples were measured by a source-measurement unit (Keythley model 236) and impedance gain/phase analyzer(SI1260, Solatron), respectively.

Figure 1 shows the I-V characteristics of the ITO/MEH-PPV/Al device. At low voltages, up to around 1 V, the current is Ohmic with a slope equal to one, while at higher voltages, the current is bulk limited with slopes $\simeq 3.3$. Figs. 2(a) and 2(b) show the frequency-dependent real and imaginary part of the dielectric constants of the ITO/MEH-PPV/Al device, respectively, calculated from the impedance data. As shown in Fig. 2(a), the real part of the capacitance does not change up to around $10^5$ Hz and relaxes around $10^6$ Hz. However, a strong frequency-dependent behavior in the imaginary part of the dielectric constants, i.e., low-frequency dispersion, is observed as seen in Fig. 2(b). This indicates that the effect on the conduction of the remaining ions used during the polymerization process of MEH-PPV is negligible, and that only the hole is a major charge carrier.[4]

We consider the potential energy configuration for the charge carriers in order to analyze the data. As we know, MEH-PPV is a $\pi$-conjugated polymer, and this kind of material can be considered as a quasi-one-dimensional semiconductor. In certain circumstances, macromolecules exhibit collective ground states induced by the interaction of their valence electrons with each other or with molecular motions of the macromolecule chains (i.e., phonons). If all the conjugation lengths were equal and electron-electron interactions were neglected, MEH-PPV would be metallic. Two phenomena can alter this metallic behavior: electron-electron interactions and electron-phonon interactions.[5] Electron-electron interactions can lower the symmetry of the electric
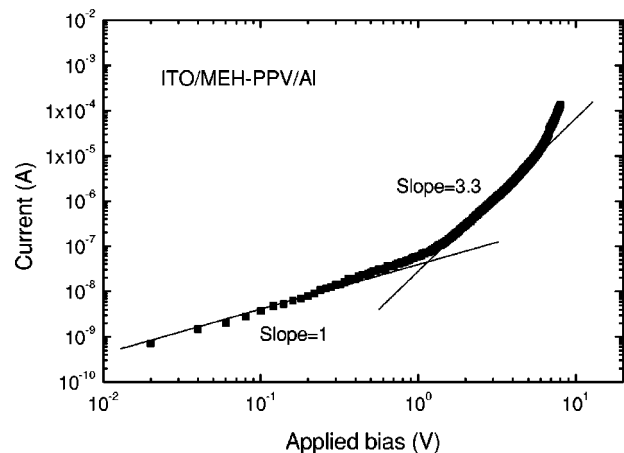


FIG. 1. Current-voltage characteristics of the ITO/MEH-PPV/Al device. The current is Ohmic at low voltages, while at higher voltages, the current is bulk limited.
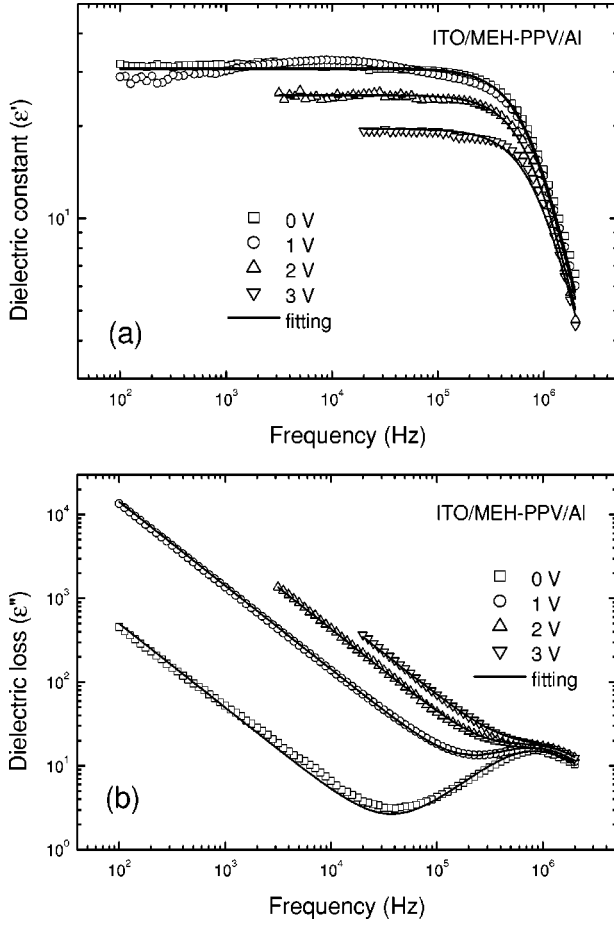
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FIG. 2. The frequency-dependent (a) real and (b) imaginary part of the dielectric constants of the ITO/MEH-PPV/Al device, calculated from the impedance data. Symbols are experimental data and lines are results of fits using Eq. (3).
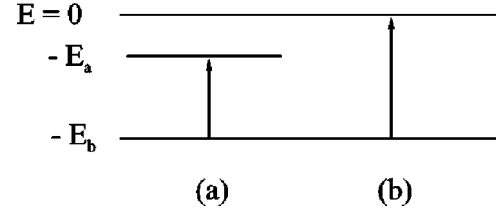


FIG. 3. The schematic energy diagram for the polaron in a conjugated polymer. $-E_b$ is the binding energy of the polaron to the potential considered above. (a) Polaron level change from $-E_b$ to $-E_a$ after charge injection. Still bounded. (b) Polaron level change from $-E_b$ to E$=0$. Free charge.

charge density, and distort the chain. The ground states with reduced-symmetry charge densities [charge-density wave (CDW)], spin densities [spin-density wave] or bond orders (bond-order-alternation waves) always exhibit decreased energies. For a given CDW, the valence-electron charge density as a function of position $x$ is given by

$$\rho(x) = \rho_o + \rho_1 \cos(qx + \Phi). \qquad (1)$$

The period $q$ of the charge-density wave is related to the number $n$ of electrons per unit length in the macromolecule by $q = n\pi$. The phase $\Phi$ is arbitrary. In addition to the charge-density wave, electron-phonon interactions lead to a symmetry-reducing distortion of the atomic geometry, which is called the Peierls transition. Therefore, the $\pi$ electrons form the polarons and the potential energy of the polaron can be thought of as periodic function as given by Eq. (1). Actually, the potential is nonperiodic because of the amorphous structure of the polymer, defects, the distribution of conjugation lengths, the distribution of charge trap sites, etc. Hence we do not use the classical particle model proposed by Grüner et al., which describes the conductivity of the density wave transport.[6] Moreover, no relaxational behavior of the charge carrier is considered in the classical particle model. Relaxational behavior of the charge carrier should be consid-

ered when we would like to describe the carrier motion in the frequency domain because of the importance of inertia.[7]

The polaron energy levels lie below the lowest unoccupied molecular orbit (LUMO) for the electrons and above the highest occupied molecular orbit for the holes. Figure 3 shows the typical schematic energy diagram for the polaron in conjugated polymers. $-E_b$ is the binding energy of the polaron to the potential well. If a charge is injected to the polaron level, the energy level of the polaron changes due to the redistribution of the charge carriers and two kinds of events can happen. Case (a) indicates that the polaron level $-E_b$ changes to $-E_a$, but it is still under the LUMO, while case (b) indicates that the polaron level $-E_b$ changes to E$=0$. In case (b), the polymer will show metallic behavior, but to our knowledge this behavior have never been observed. This indicates that the Peierls instability will not be broken because of the amount of the injected charges in our experiments. Therefore, one can say that the polarons pass through the polymer under the influence of the potential due to the CDW and Peierls instability by a hopping.[8]

The behavior of the polarons is composed of the dc and low-frequency diffusive motion under the influence of an external applied field, and of high-frequency oscillatory motion under the internal potential. Then the equation of motion for hopping polarons can be described as a generalized Langevin equation that holds for arbitrary frequencies and that is based on the memory function formalism for the relaxational behavior of the carrier:[9]

$$m\langle \ddot{x} \rangle + m\Gamma \langle \dot{x} \rangle + m\omega_o^2 \tau \int_{t_o}^t M(t-t')dt' = K(t). \qquad (2)$$

Here, m and $x$ are the effective mass and the position of a charge carrier, $\Gamma$ is a damping constant, $\omega_o$ is a phonon frequency, M(t) is a memory function, and K(t) is an external oscillation field. In Eq. (2), $\langle \cdots \rangle$ represents an ensemble average. The random force in the generalized Langevin equation disappeared during the ensemble average process. In an extreme case [M(t) is zero or unity] Eq. (2) becomes a diffusion equation or a damped harmonic equation. The frequency-dependent complex conductivity $\sigma^*(\omega)$ and complex dielectric constant $\epsilon^*(\omega)$ can be obtained from the solution of Eq. (2) with the help of the relation between the conductivity and the dielectric constant $\sigma(\omega) = (\omega/4\pi i)[\epsilon(\omega) - \epsilon_\infty]$,

$$\epsilon^* = \epsilon_\infty - \frac{4\pi e^2 n}{m} \frac{1}{\omega^2 + i\omega\Gamma + i\omega\omega_o^2 M(\omega)}. \qquad (3)$$

TABLE I. Fitting parameters used in this model at each dc bias voltages.

| $V$ | $\tau$ | $\Gamma$ | $4\pi e^2 n/m$ |
|---|---|---|---|
| 0 | $6.0\times10^{-4}$ | $2.0\times10^{21}$ | $5.0\times10^{28}$ |
| 1 | $2.2\times10^{-5}$ | $5.5\times10^{22}$ | $1.5\times10^{30}$ |
| 2 | $7.0\times10^{-6}$ | $1.9\times10^{23}$ | $4.9\times10^{30}$ |
| 3 | $3.8\times10^{-6}$ | $3.5\times10^{23}$ | $8.9\times10^{30}$ |

Here $e$ and $n$ are the charge and the concentration of a charge carrier, and $M(\omega)$ is a memory function in frequency domain. Usually $M(t)$ is assumed to be a single exponential. The relationship between $M(\omega)$ and $M(t)$ is

$$M(\omega)=\mathcal{F.T.}[M(t)=A\cdot\exp(-t/\tau)]=\frac{1}{1+i\omega\tau}, \quad (4)$$

where $\tau$ is the transition time from the low-frequency diffusive motion to the high-frequency oscillatory motion and $\mathcal{F.T.}$ denotes for the Fourier transformation. $A$ is a normalization constant to satisfy the constraint condition of the memory function. The solid lines in Figs. 2(a) and 2(b) are the fitting results using Eq. (3). We used only three parameters, $n$, $\Gamma$, and $\tau$, to fit the dielectric data, and the dielectric constant and the dielectric loss are fitted by the same values of the parameters for the same dc bias voltage, and the experimental data are well fitted over four decades. The fitting parameters are listed in Table I.

As shown in Table I, the fitting parameters show a strong voltage dependence. The mobility of the charge carriers in the $\pi$-conjugated polymers can be described by[10]

$$\mu(E)=\mu(0)\exp(a\sqrt{E}), \quad (5)$$

where $\mu(0)$ denotes the mobility at zero field. The transition time $\tau$ and the damping constant $\Gamma$ in the generalized Langevin equation are highly related to the mobility, and thus these parameters are thought to depend on the same function of voltage. By analogy of these results, the bias voltage dependence of parameters $\Gamma(V)$ and $\tau(V)$ are assumed as follows:

$$\Gamma(V)=\Gamma(0)\exp(\alpha\sqrt{V}), \quad (6)$$

$$\tau(V)=\tau(0)\exp(\beta\sqrt{V}). \quad (7)$$

Figure 4(a) shows the voltage dependence of fitting parameters $\Gamma$ and $\tau$. Symbols in the figure represent parameters at each dc bias voltage and solid lines are fitting results. The parameters $\alpha$ and $\beta$ are 3.05 and $-2.98$, respectively.

For the charge-carrier concentration n, voltage-dependent current density of the EL device using MEH-PPV should be considered. If the barrier to carrier injection at one of the injecting electrodes is less than 0.3–0.4 eV, the conduction in single layer organic LED's will be bulk limited, and the $I$-$V$ characteristics of the $\pi$-conjugated polymer can be fitted to a power law $J=KV^{m+1}$.[2] Since the current density $J$ is equal to $ne\mu\cdot E$, the voltage-dependent charge-carrier concentration n(v) can be obtained by,

$$n\propto\frac{V^{m+1}}{e\mu E}\propto\frac{b'\cdot V^m}{\mu}=\frac{b\cdot V^m}{\exp(a\sqrt{V})}. \quad (8)$$
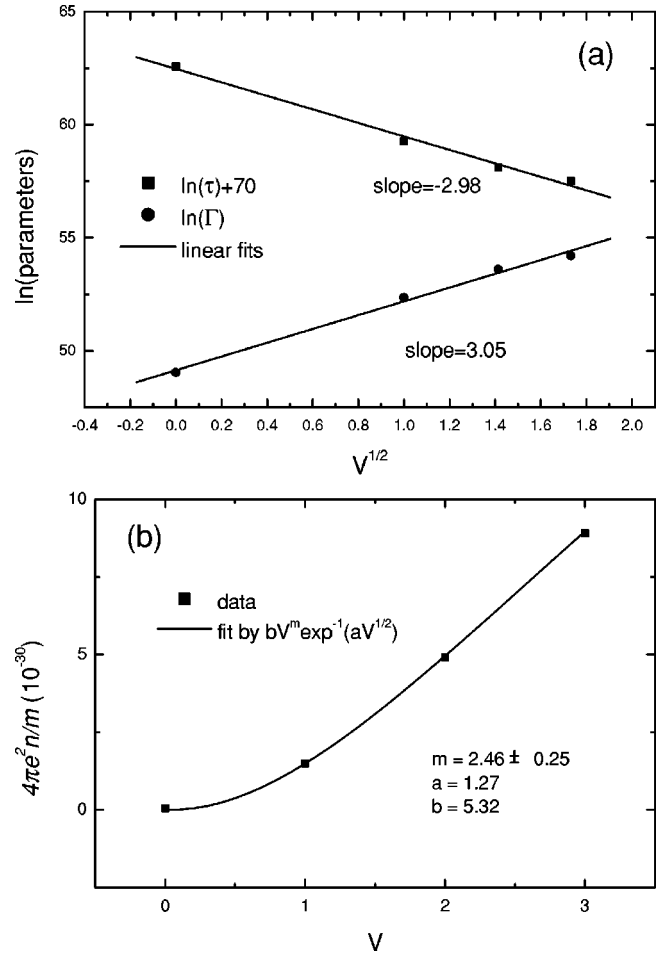


FIG. 4. The voltage dependence of fitting parameters used in our model. Symbols in the figure represent parameters at each dc bias voltage and solid lines are fitting results.

Figure 4(b) shows the voltage dependence of the charge-carrier concentration $n$ used in our model. Symbols in the figure represent experimental data at each dc bias voltage and the solid line is the result of using Eq. (8) for a fit. The parameters a, b, and m are 1.27, 5.32, and 2.46±0.25, respectively.

From the analysis, the conduction of the charge carriers is governed not only by the applied field but also by the potential configuration ($\Gamma$ and $\tau$ are the characteristic parameters) of the charge carriers. As we have seen in Fig. 2(b), the imaginary part of the dielectric constant shows dielectric dispersion at low frequencies and a dielectric loss peak at higher frequencies, simultaneously. There are several conduction models[11] but they cannot explain the two phenomena simultaneously. The phenomenological equations such as Debye, Cole-Cole, Cole-Davidson, and Wiliam-Watt equations only can fit the loss peak at the high-frequency side. The generalized Langevin equation is the only one that can fit the low-frequency dispersion and the high-frequency loss peak simultaneously to our knowledge, and it is revealed that only one conduction mechanism, hopping conduction, can show both low-frequency dispersion and high-frequency loss peak, simultaneously.

Another interesting point is the following. In this model, the $\tau$ is the transition time from diffusive motion to oscilla-

tory motion, i.e., for time scales longer than $\tau$, the charge carrier shows diffusive motion while for the shorter time scales, it shows oscillatory motion. If the material is amorphous and the potential energy has some kind of distribution, the transition time $\tau$ also should have a similar kind of distribution. However, the single transition time $\tau$ could fit the whole data satisfactorily. This is an unexpected result, and a possible explanation is that the actual hopping sites have the same (or very similar) environmental conditions such as potential energy, hopping distance, etc., even though the quasi-one-dimensional conduction paths of $\pi$-conjugated polymers are not parallel. It seems that the macroscopically amorphous character cannot change the microscopic electronic structure of the polymeric material. We think this result is unexpected and needs more study.

In summary, the generalized Langevin equation was used to analyze the dielectric behavior in the frequency domain, and the experimental data were satisfactorily fitted by the generalized Langevin equation. We observed voltage dependence of the fitting parameters used in our model, and appropriate fitting functions were proposed. It is confirmed that the fitting results of the parameters follows well to the corresponding functions we proposed. From the analysis, we determined the signature of the bulk limited conduction. It also was confirmed that the electric current at arbitrary frequency is governed by several intrinsic voltage-dependent parameters, $\Gamma$, $\tau$, and $n$. We think the generalized Langevin analysis is a very good approach to understand the charge transport in the frequency domain.

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*Electronic address: kimsh@etri.re.kr

[1] D.D.C. Bradley, A.R. Brown, P.L. Burn, R.H. Friend, A.B. Holmes, and A. Kraft, *Electronic Properties of Polymers*, Springer Series in Solid State Sciences, Vol. 107 (Springer-Verlag, Heidelberg, 1992), pp. 304–309.

[2] A.J. Campbell, M.S. Weaver, D.G. Lidzey, and D.D.C. Bradley, J. Appl. Phys. **84**, 6737 (1998).

[3] S.H. Kim, Y.H. Hwang, J.A. Kim, Y.S. Yang, B.G. Chae, and M.S. Jang, J. Appl. Phys. **85**, 347 (1999).

[4] S.H. Kim, Y.S. Yang, H.J. Kim, N.Y. Ryu, and M.S. Jang, Ferroelectrics **196**, 261 (1997).

[5] C.C. Ku and R. Liepins, *Electronic Properties of Polymers, Chemical Principles* (Hanser, Munich, 1987), Chap. 5.

[6] G. Grüner, W.G. Clark, and A.M. Portis, Phys. Rev. B **24**, 3641 (1981).

[7] A.K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics, London, 1983), p. 37.

[8] E.M. Conwell and M.W. Wu, Appl. Phys. Lett. **70**, 1867 (1997); V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, and H. Bässeler, J. Appl. Phys. **84**, 848 (1998); J.C. Scott, S. Karg, and S.A. Carter, *ibid.* **82**, 1454 (1997).

[9] P. Brüesch, S. Strssler, and H.R. Zeller, Phys. Status Solidi A **31**, 217 (1975).

[10] D.M. Pai, J. Chem. Phys. **52**, 2285 (1970); P.W.M. Blom, M.J.M. de Jong, and M.G. van Munster, Phys. Rev. B **55**, R656 (1996); H. Meyer, D. Haarer, H. Naarmann, and H.H. Hörhold, *ibid.* **52**, 2587 (1995).

[11] H.N. Nagashima, R.N. Onody, and R.M. Faria, Phys. Rev. B **59**, 905 (1999); K. Ito, Y. Tanabe, K. Akagi, and H. Shirakawa, *ibid.* **45**, 1246 (1992); C.M. Lepienski, R.M. Faria, and G.F. Leal Ferreira, Appl. Phys. Lett. **70**, 1906 (1997); W. Rehawald, H. Kiess, and B. Binggeli, Z. Phys. B: Condens. Matter **68**, 143 (1987).